



## MECHANICAL PERFORMANCE OF GEOPOLYMERIC MORTARS BASED ON TUNISIAN CALCINED CLAY, FLY ASH AND METAKAOLIN

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**Key words:** Geopolymeric mortars, infrastructure repair, compressive strength, shrinkage, hydration products

**Abstract:** *Infrastructure rehabilitation represents a multitrillion dollar opportunity for the construction industry. Since the majority of the existent infrastructures are Portland cement concrete based this means that concrete infrastructure rehabilitation is a hot issue to be dealt with. Geopolymers are novel inorganic binders with high potential to replace Portland cement based ones. So far very few studies in the geopolymer field have addressed the rehabilitation of deteriorated concrete structures. This paper discloses results of an investigation concerning the development geopolymeric repair mortars. The mortars are based on Tunisian clay coming from Medenine region, plus calcium hydroxide, sodium silicate and sodium hydroxide. Results show that the geopolymeric mortar has a high compressive strength and a lower unrestrained shrinkage performance as long as partial replacement by metakaolin is carried out. The results also show that Tunisian calcined clay based mortars have hydration products with typical geopolymeric phases.*

### Introduction

Worldwide infrastructure rehabilitation costs are staggering. For example in the USA the needs are estimated to be over 1.6 trillion dollars the next five years [1]. Many of the degraded concrete structures were built decades ago when little attention was given to durability issues [2]. Materials with low durability require frequent maintenance and conservation operations or even its integral replacement, being associated with the consumption of raw materials and energy. The patch repair method is widely used to restore the original conditions of the concrete structures [3, 4]. Most patch repair mortars fall into two categories, the mortars based on organic binders (epoxy resin or polyester) or those based on inorganic binders like Portland cement. The former are associated with toxic side effects [5] and they are known for its high carbon footprint [6]. Geopolymers are novel inorganic binders with high potential to replace Portland cement based ones [7]. The geopolymerization of alumino-silicate materials is a complex chemical process evolving dissolution of raw materials, transportation or orientation and polycondensation of the reaction products [8-10]. Investigations in the field of geopolymers reveal a third category of mortars with high potential to be used in the field of concrete patch repair. Some authors [11] have shown that concrete specimens repaired with geopolymeric mortar with 1 day curing have higher bond strength than specimens repaired with current commercial repair products after 28 days curing. This is a promising

performance because adhesion to the concrete substrate is a crucial property of the repair mortars [12]. This paper presents experimental results of an investigation concerning the development geopolymeric repair mortars based on a Tunisian clay. The influence of the partial replacement of Tunisian clay by fly ash and metakaolin on the mechanical performance of the repair mixtures is analyzed.

## Experimental work

### Materials

The clay materials used were from Medenine Region of Tunisia. Previous studies showed that kaolinite is the major mineral and quartz the major impurity in the studied clay [13]. The dried clay fractions were crushed in a crusher apparatus and then sieved to 100  $\mu\text{m}$  mesh. The clay fractions were calcined in a programmable electric furnace (Nabertherm, Mod.LH 60/14) for 6 h at a heating rate of 11.33 C/min at the following temperature 700 °C. Metakaolin was obtained from Barqueiros (origin company of mining) in Portugal and the fly ash was supplied by (origin place,type C). Table 1 gives their composition as detected by X-ray fluorescence (XRF).

Table 1. Chemical composition of raw material (%).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
Clay	60.8	16.2	2.15	5.87	0.08	0.003	2.38	2.71	-	-
MK	50.5	42.6	2.28	0.157	0.215	2.75	0.241	0.04		
	0.207	0.807								
FA	56.0	26.0	6.6	2.10	1.24	-	0.56	2.35	1.18	-

Figure.1 shows the results of X-ray diffraction analysis using an ARL 9900 series workstation (Thermal Scientific) with Co-K $\alpha$  radiation (generated at 40 kV, 40 mA), scanning at a rate of 2.4°/min. In Figure. 1 it is clear that metakaolin is largely amorphous, with a small quantity of quartz as an impurity phase, and a small amount of residual kaolinite. The fly ash used contains large amounts of quartz phases in addition to the main amorphous phase. Figure 2 (a) Shows the surface morphologies of the fly ash in comparison with the metakaolin (MK).

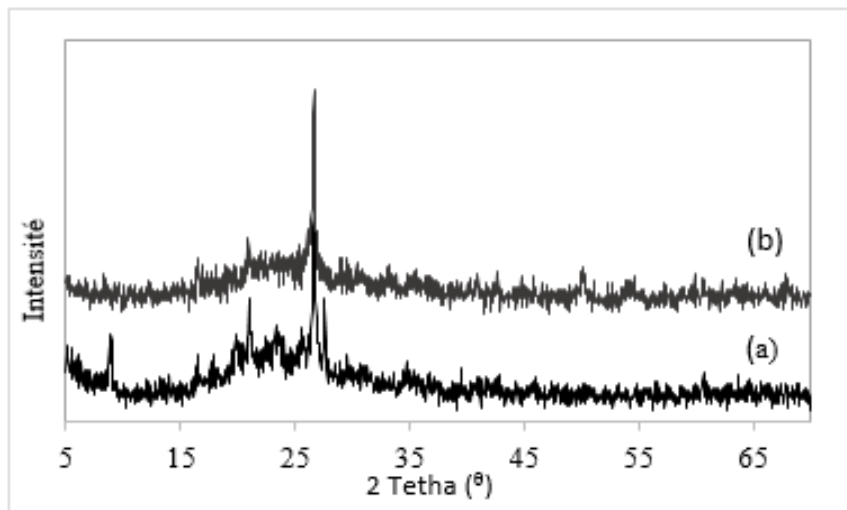
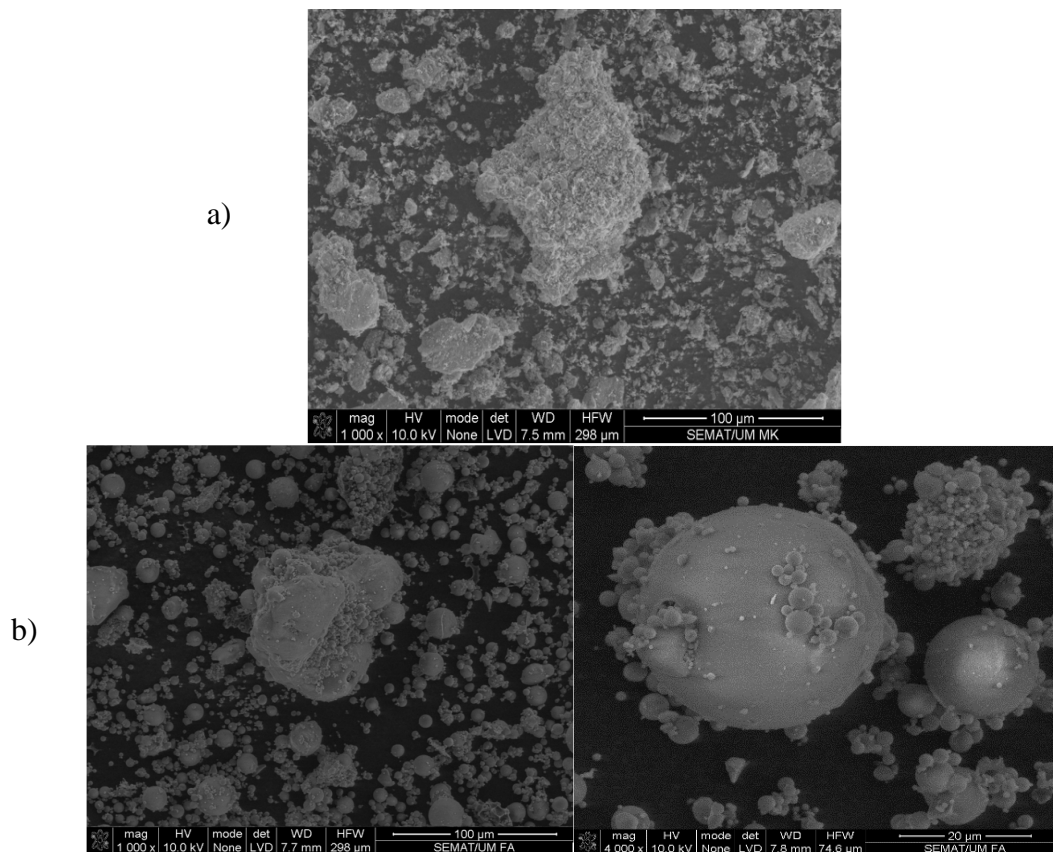


Figure 1. X-rays diffractograms of the MK (a) and the FA (b)



**Figure 2.** Scanning electron microscope (SEM) of (a) fly ash and (b) metakaolin

It can be seen that the fly ash mainly consists of spherical particles with smooth outer surfaces. The smooth aluminosilicate spherical particles, also known as cenospheres, are formed as a result of thermochemical transformations of mineral particles during coal combustion process, where the minerals melt to form small droplets, which upon sudden cooling and action of surface tension forces adopt the spherical shape [14]. Also, the figure 2 (b) revealed the morphology of the metakaolin.

#### Geopolymeric mortar preparation

In order to improve the mechanical performance of the mixtures previously tested [13] the Tunisian clay was partially replaced by fly ash and metakaolin. The percentages of FA were 10% and 15% as well as the percentages of MK were 10%, 15% and 30%. The reference geopolymer mortar named G1R3 was composed by 1264.79 g of calcined clay, 140.53g of lime (10%), 4215.97g of sand, 801.91g of  $\text{Na}_2\text{SiO}_3$  and 322.29 g of NaOH with an activator/binder mass ratio of 80%. The alkaline solution used was a mixture of aqueous solution of sodium hydroxide 12 M and sodium silicate with bulk density of  $1350 \text{ kg/m}^3$  with ratio:  $\text{Na}_2\text{SiO}_3 / \text{NaOH} = 2.5$ . The sodium hydroxide solution was obtained by dissolving dried pellets of 99% purity in distilled water. The sodium silicate solution had a composition by weight  $\text{Na}_2 (\text{SiO}_2)_x \cdot y (\text{H}_2\text{O})$ . With  $3.19 \leq x \leq 3.53$  and  $50 \% \leq y \leq 60 \%$ . The geopolymer mortar (G1R3 with FA/MK mixture and liquid alkaline activator) was mixed thoroughly for 10 min in a mixer and transferred to plastic molds. The molds were covered with a thin plastic film to avoid water evaporation and then kept for 24 h at the ambient atmosphere of the laboratory ( $24^\circ\text{C} - 26^\circ\text{C}$ ). The reported results were the average of three samples for each test.

### Mechanical properties testing

The compressive strength and flexural strength was obtained using 160×40×40 mm<sup>3</sup> prismatic specimens according to EN 1015-11. The modulus of elasticity was determined using cylindrical moulds for the geopolymeric sample with (diameter: 5 cm; length: 10cm). These specimens were tested after 28 curing days.

### Unrestrained shrinkage testing

Unrestrained shrinkage used prismatic specimens measuring 25×25×250 mm<sup>3</sup> and was determined according to LNEC E389-1993. The specimens are removed from molds 24 h after being mixed and placed, then they are wrapped with Perspex paper. Other authors used aluminum paper, having reported the formation of hydrogen gas bubbles due to a reaction between the aluminum and the alkalis from the mortar [15]. The measurement of shrinkage was carried out on hardened geopolymer cylinder paste samples aged of 1, 7, 14, 21 and 28 days respectively.

### FTIR

The FTIR spectra were acquired in the attenuated total reflectance mode (ATR), between 4000 and 550 cm<sup>-1</sup>, using a Perkin Elmer FTIR Spectrum BX with an ATR PIKE MIRacle Specimens for FTIR study were prepared by mixing 1mg of sample in 100 mg of KBr as suggested by Zhang et al. [16]. Spectral analysis was performed over the range 4000–400 cm<sup>-1</sup> at a resolution of 4cm<sup>-1</sup>

## Results and discussion

### Mechanical properties

Figure 3 shows the compressive and flexural strength and modulus of elasticity of the new mixtures. The results show that the partial replacement of Tunisian clay by 10% or even 15% of fly ash is not advantageous for 28 days compressive strength. The same occurs for flexural strength, although the 15% fly ash mixture shows a minor increase when compared to the reference mixture. This behavior is related to the low reactivity of fly ash. In the geopolymeric mixtures in which the Tunisian clay was partially replaced by metakaolin an increase in compressive strength is visible only for 15% and 30% percentages. This however is not reflected in terms of flexural strength. This maybe explained by the different shrinkage performance of the different mixtures just because a higher shrinkage is usually associated to a lower flexural strength. The replacement of Tunisian clays by 15% and 30% metakaolin allows for compressive strengths around 30 MPa which are typical of old OPC reinforced concrete structures and constitute an important compressive strength requirement for repair mortars. The results show that the modulus of elasticity increases slightly with the replacement of Tunisian clay by fly ash. This behavior is not influenced when the fly ash percentage increase from 10% to 15%. A higher modulus of elasticity is associated with the replacement of Tunisian clay by metakaolin. This behavior is partially related to the increased in the compressive strength.

### Unrestrained shrinkage

Figure 4 shows the results of unrestrained shrinkage. In the first two days the shrinkage increases very rapidly for the six geopolymeric mixtures. The rapid increase of unrestrained shrinkage has to do with the capillary tensions within the gel framework during geopolymerization process [17]. The maximum unrestrained shrinkage is around 500 to 600 microstrain. This constitutes a reduction to the previous reported maximum unrestrained shrinkage [13] being due to the reduction of the alkaline activator.

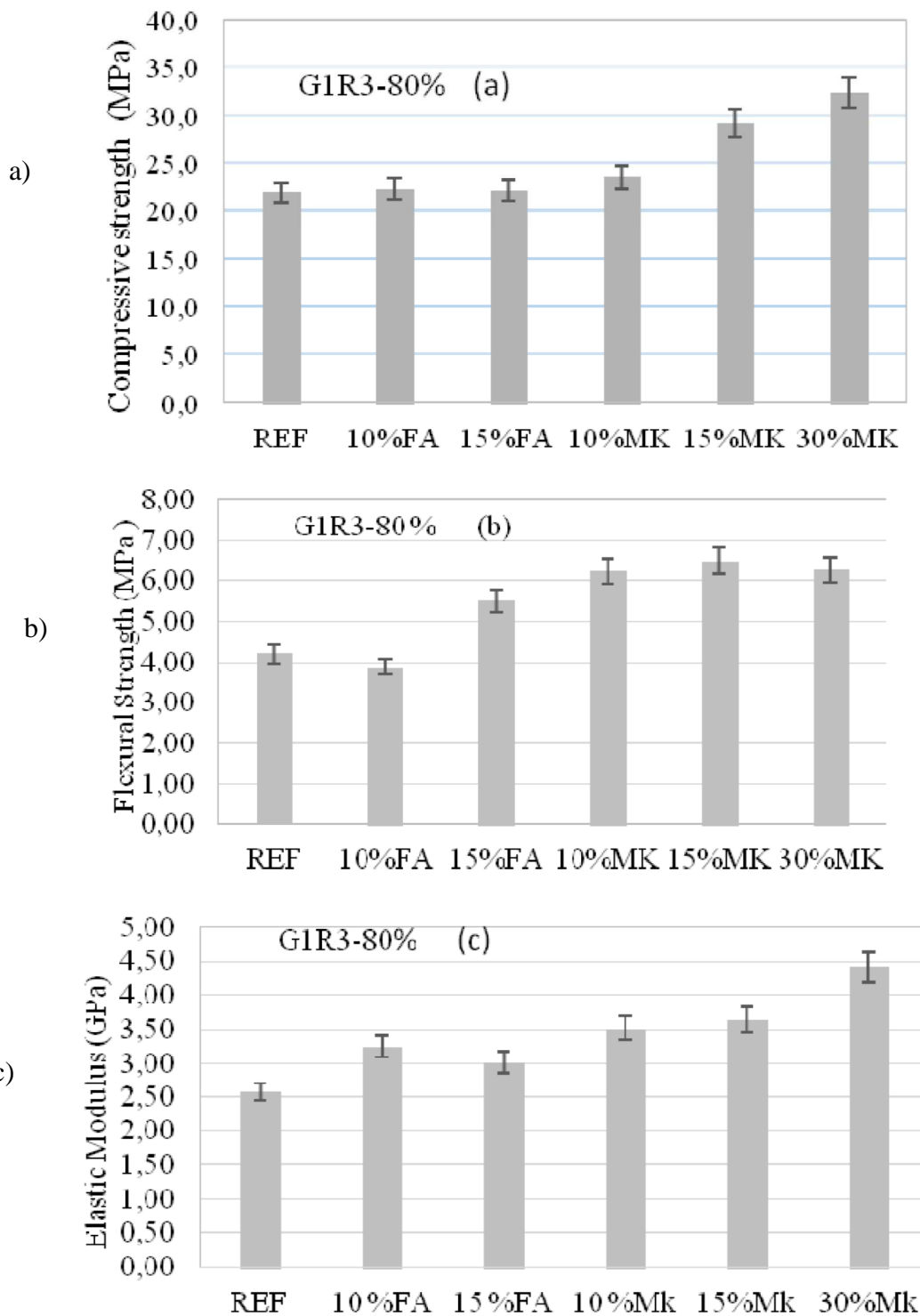


Figure 3. Compressive flexural , Flexural strenght : (a),(b) and Elastic modulus : (c) for geopolymeric mortar mixtures with sodium hydroxide concentrations (12 M) and sand/binder mass ratio (R = 3) and with ratio Activator/Binder (R= 80 %) with different percentage of metakaolin and fly ash added to G1R3 after 28 days time of curi

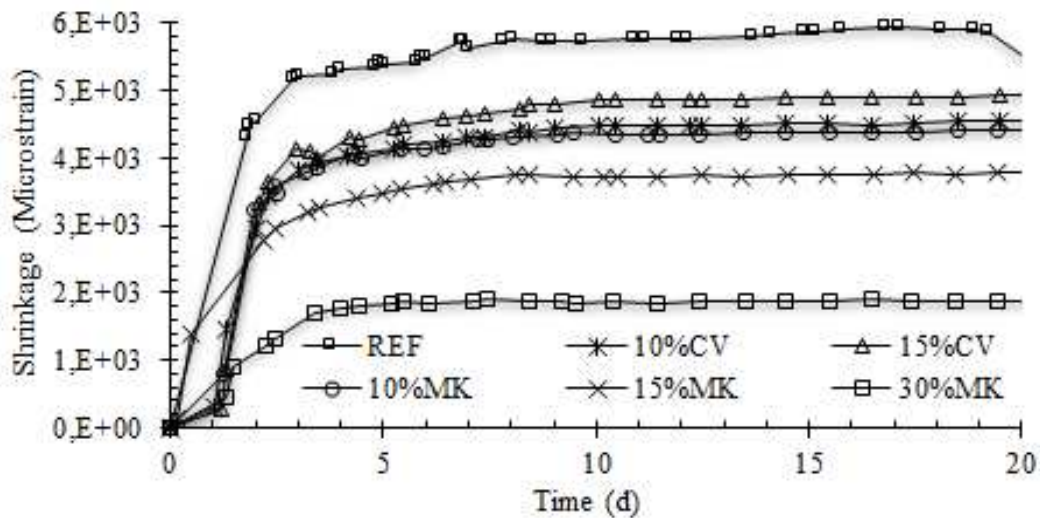


Figure 4. Shrinkage of the geopolymer mixture as function of curing time (days)

This maximum is similar to the one reported by others [18] based on alkali activated metakaolin.

The unrestrained shrinkage results confirm that the mixtures with higher flexural strength have lower unrestrained shrinkage. The partial replacement of Tunisian clay by fly ash also leads to a lower unrestrained shrinkage performance than the reference mixture. Partial replacement by metakaolin outperforms fly ash based mixtures. The comparison of the unrestrained shrinkage in 15% fly ash mortar and in 15% metakaolin shows a very relevant difference. When 30% metakaolin is used a very low unrestrained shrinkage is observed. Since mortars required for OPC patch repair require very low unrestrained shrinkage [19] this means that new geopolymeric mortar mixtures based on the partial replacement of Tunisian clay by metakaolin have an acceptable performance concerning this parameter.

#### Hydration products

The FTIR spectra of the hardened Tunisian clay geopolymer mortars are presented in Figure 5. Strong vibration typical of aluminosilicates can be seen. The peak centered around  $975\text{ cm}^{-1}$  shifts to a lower value, and this shift is characteristic of a geopolymerization reaction corresponding to the Si-O-Al and Si-O-Si vibration bands. The band at about  $870\text{ cm}^{-1}$  assigned to Si-OH bending vibration. Al-O-Si vibrations corresponding to the absorption bands  $600\text{--}800\text{ cm}^{-1}$ . The absorption peak of  $782\text{ cm}^{-1}$  was an indication of the presence of quartz [20]. The absorption band around  $1413$  and  $1433\text{ cm}^{-1}$  is attributed to stretching vibrations of  $\text{CO}_3^{2-}$  ions confirming the existence of carbonate species [21]. Atmospheric  $\text{CO}_2$  enters in geopolymer to react with unhydrated sodium to form sodium carbonate. A peak assigned to water appears at  $1645\text{ cm}^{-1}$ . These bands decrease in intensity in the geopolymer paste after curing process. The decreasing in the OH bond may be also due to the zeolites structure of zeolites (crystalline phase) that needs more water molecules than the minerals polymers (amorphous phase). Fig 6 shows the Fourier transform infrared spectra of geopolymers of G1R3 modified mixtures. All FTIR spectra involved in a single band located at  $1000$  and  $1004\text{ cm}^{-1}$ , corresponding to a region assigned for Si-O-Si [22-24]. The presence of the bands located at  $776\text{ cm}^{-1}$  and at  $692\text{ cm}^{-1}$  are due to the quartz [25]. The small bands appearing at around  $1420, 1422\text{ cm}^{-1}$  and at  $1489\text{ cm}^{-1}$  are related to the asymmetric stretching of the O-C-O bonds of  $\text{CO}_3^{2-}$  due to atmospheric carbonation for all geopolymer mortars.

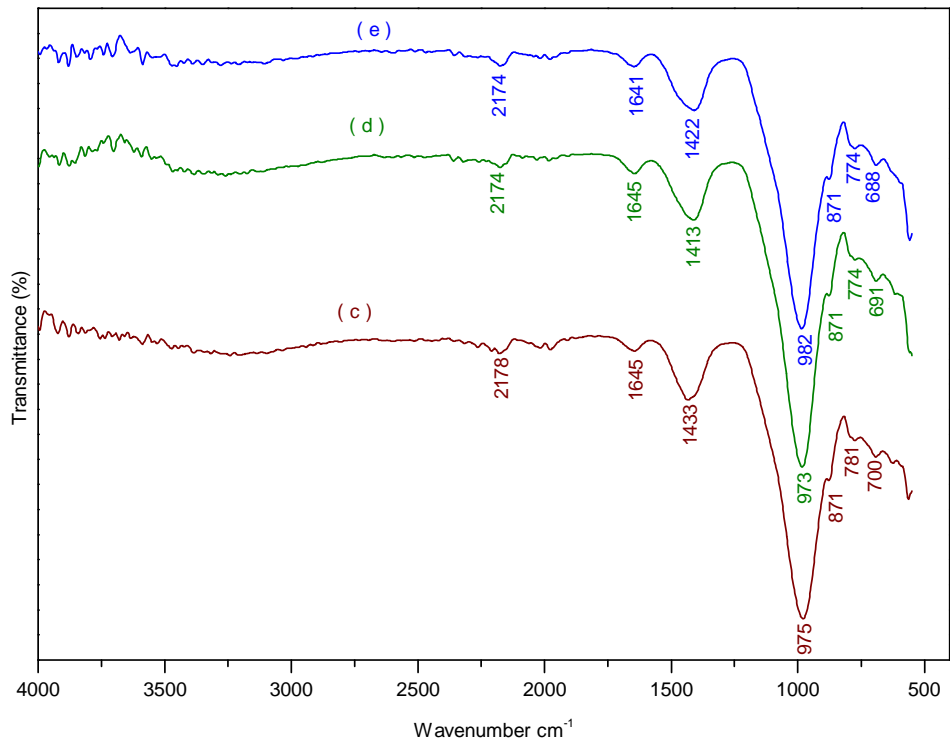
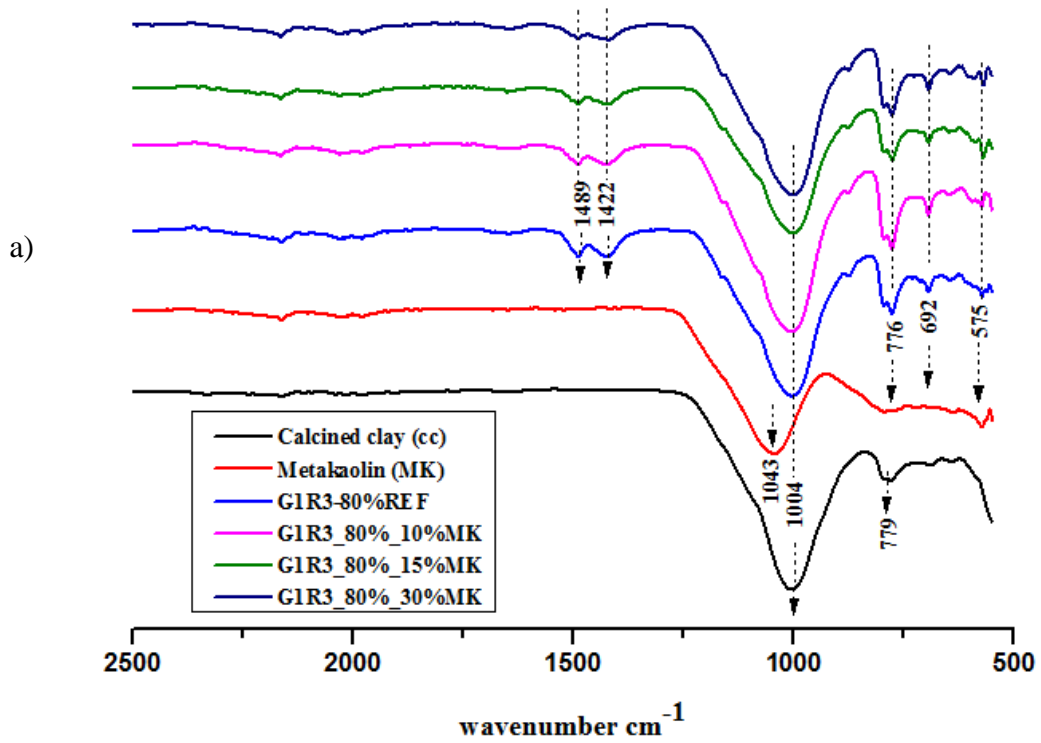


Figure 5: FTIR spectra of the geopolymer mortar (c) G1R2, (d) G1R3 and (e) G1R4



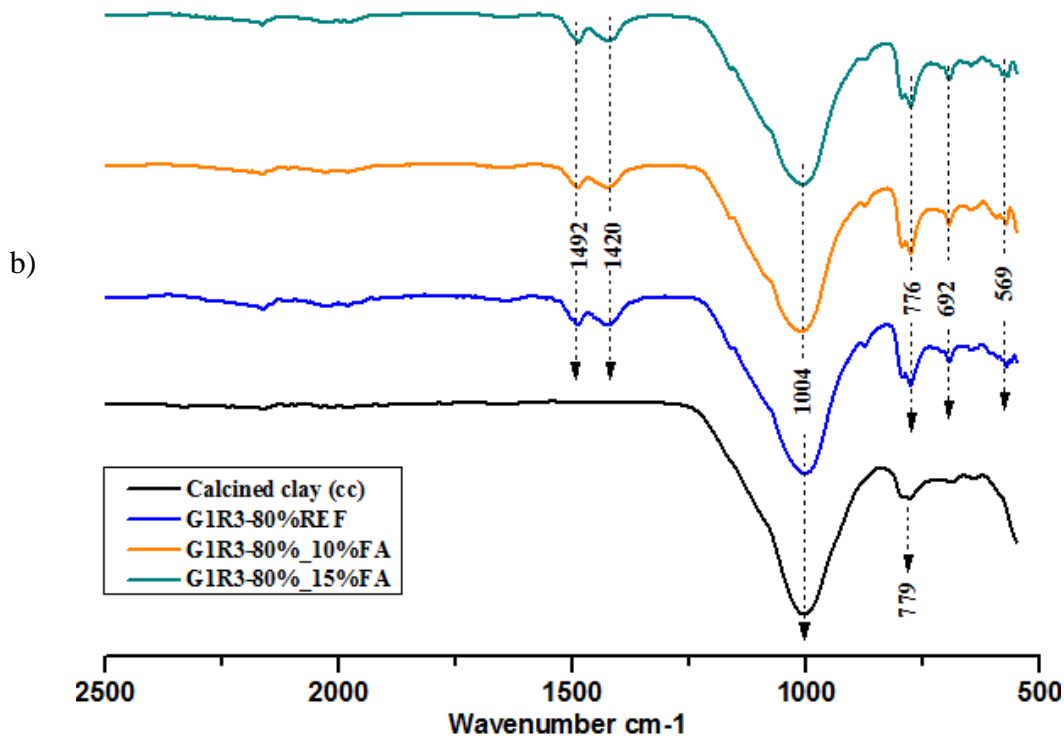


Figure 6: Fourier transform infrared spectra of of geopolymers of G1R3 modified mixtures: a) metakaolin based; b) fly ash based

### Conclusions

This paper presents experimental results of an investigation concerning the development geopolymeric repair mortars based on a Tunisian clay. The influence of the partial replacement of Tunisian clay by fly ash and metakaolin on the mechanical performance of the repair mixtures is analyzed. The following conclusions can be made. The replacement of Tunisian clays by 15% and 30% metakaolin allows for compressive strengths around 30 MPa which are typical of old OPC reinforced concrete structures and constitute an important compressive strength requirement for repair mortars. The modulus of elasticity increases slightly with the replacement of Tunisian clay by fly ash and in a higher extension when metakaolin is used. The reduction of the alkaline activator/binder mass ratio to 80% of the former mixtures led to a relevant reduction in the shrinkage performance. The partial replacement of Tunisian clay by fly ash also leads to a lower shrinkage performance than the reference mixture. Partial replacement by metakaolin outperforms fly ash based mixtures. Since mortars required for OPC patch repair require very low unrestrained shrinkage this means that new geopolymeric mortar mixtures based on the partial replacement of Tunisian clay by metakaolin have an acceptable performance concerning this parameter.

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